

Report for 2001MA2301B: Sources and Behavior of Copper-Binding Compounds in Rivers and Estuaries

There are no reported publications resulting from this project.

Report Follows:

Sources and Behavior of Copper-Binding Compounds in Rivers and Estuaries

Problem and Research Objectives

Concentrations of copper in effluents from publicly-owned treatment works and other dischargers in Massachusetts regularly exceed permitted levels. It is generally agreed that current water quality criteria for copper, based on laboratory toxicity tests, are often stricter than intended by regulatory guidelines. The main reason for this is that complexation (binding) of copper by naturally present dissolved organic compounds decreases bioavailability of copper, resulting in lower toxicity in the natural waters than would be observed in the laboratory tests. Conducting toxicity tests in individual receiving waters to develop site-specific water quality criteria is possible, but prohibitively expensive. The U.S. Environmental Protection Agency (EPA) Office of Water has therefore supported the development of a chemical-biological model predicting copper toxicity in a given water as a function of easily measurable chemical parameters including pH, concentration of dissolved organic carbon, and concentrations of major ions such as calcium, magnesium, and sulfate. The EPA, the Massachusetts Department of Environmental Protection (MADEP) and other states' regulatory agencies, as well as the region's dischargers, are all interested in the speedy validation of this "Biotic Ligand Model" as a low-cost technique for developing site-specific water quality criteria for copper.

The Biotic Ligand Model's ability to produce accurate predictions of copper toxicity in an effluent-receiving water depends on its ability to predict the extent of copper complexation in that water. The model assumes that humic substances, the biologically refractory degradation products of higher plants, are both the copper-binding compounds (ligands) controlling complexation and the main constituents of the dissolved organic carbon present in surface waters. However, other compounds less abundant than humic substances have been shown to be more significant copper complexing agents in a variety of natural waters. In addition, other organic compounds may constitute a significant fraction of the dissolved organic carbon, especially in estuaries and sewage effluents. The assumptions of the Biotic Ligand Model may therefore lead to both overestimates or underestimates of the actual toxicity of copper in a given water. The goal of our study was to examine the behavior of copper-binding compounds in a sewage-effluent impacted river, in a relatively unimpacted estuary, and in highly impacted estuaries in order to determine whether the assumptions made by the Biotic Ligand Model will lead to reasonable predictions of copper toxicity in these systems or whether other factors need to be taken into account.

Methodology

a. Field Sites

1. *Sewage-effluent impacted river.* Field samples were collected from the Taunton River watershed in Massachusetts. This part of the project was conducted in close collaboration with an ongoing project by the environmental consulting firm ENSR, whose goal was to validate the Biotic Ligand Model in this watershed.

Grab samples of discharge of three POTW's (Bridgewater, Mansfield and Middleborough, MA), receiving waters upstream of the POTWs, and Taunton River samples were collected during ENSR sampling campaigns under both low-flow and high-flow conditions in acid-washed

Teflon bottles using “clean hands/dirty hands” trace-metal clean sampling techniques. A YSI Model 6920 multi-parameter water quality monitor was used to measure temperature, specific conductivity, pH, dissolved oxygen, and turbidity in the water before sampling. Additional ancillary measurements needed as input to the Biotic Ligand Model (DOC, calcium, magnesium, chloride, sodium, potassium, alkalinity, sulfate and sulfide) were performed by ENSR’s subcontractors and provided to us.

2. *Unimpacted estuary.* Water samples from the Saco River estuary across a salinity transect were collected in acid-washed Teflon bottles from a small aluminum boat or a polyethylene kayak. For copper speciation measurements, 1-2 liter samples of surface water were collected from upstream of the boat to minimize copper contamination of samples. Samples for DOC measurements were also collected upstream of the boat, syringe-filtered using pre-combusted glass syringes and pre-rinsed polysulfone cartridge filters, acidified, and stored in the refrigerator in pre-combusted glass vials. Temperature, chlorophyll, dissolved oxygen, turbidity and salinity were measured at each sampling site using a Hydrolab Datasonde.

3. *Impacted estuaries.* Samples were collected near the University of Rhode Island dock in Narragansett Bay, near docks of Waquoit Bay and Eel Pond on Cape Cod, and 100 meters offshore in Quincy Bay and Dorchester Bay (both in Boston Harbor), using the same techniques as for the Saco River.

b. Sample Storage

Samples for copper were kept on ice during transport to the laboratory, where they were quick-frozen in liquid nitrogen for storage. We have found that this quick-freezing technique eliminates artifacts sometimes associated with freezing of samples, especially coagulation processes. After thawing, samples were either analyzed without filtering, or were syringe-filtered through 0.2 μm polycarbonate membrane filters (Nucleopore, 47 mm filter diameter) sandwiched in polycarbonate filter holders. For some of the samples from impacted estuaries, subsamples of this 0.2 μm filtrate (dissolved fraction) were filtered again through 0.02 μm pore size inorganic membrane cartridge filters (Anatop-25, 22 mm filter diameter). The filters were acid-cleaned and rinsed with DDW before use. Filter controls indicated that contamination of samples with copper and copper-binding compounds was negligible.

c. Sample Analysis

The content of copper-binding compounds in our samples was analyzed using the competitive ligand exchange adsorptive cathodic stripping voltammetry titration techniques described in our previous works^{1,2}. We have made two significant improvements over more commonly used approaches. First, we used *overload* titrations¹ for accurate calibration of the technique in each sample. Second, we quantified copper bound by *kinetically inert* compounds using very high quantities of competing ligand. Furthermore, we have calibrated the competing ligand, salicylaldoxime, for use in a range of salinity and pH values. Previous works have only used salicylaldoxime in seawater systems.

Principal Findings and Significance

1. *Sewage effluent impacted river.* The ENSR study determined that copper toxicity was well predicted by the Biotic Ligand Model in these systems. However, the results of our part of this study were inconclusive. Both the sewage effluents and the receiving waters contained a high quantity of surfactants, which interfered with the voltammetric technique. Most of the interferences we observed were not reproducible, so even attempts to calibrate the technique for surfactant effects remained generally unsuccessful.

2. *Unimpacted estuary.* The content of ligands we found in the highest salinity sample (salinity 27.6) of a winter transect of the Saco river corresponded to what would be expected if the ligands from lower salinity samples (salinities 0.5 and 20.4) were diluted with ligand-free seawater. The copper-binding ability of these ligands per mg DOC corresponded closely to the copper-binding ability of standard humic substances isolated from the Suwannee River in Georgia. This finding indicates conservative dilution of riverine humic ligands with no significant contribution of the seawater endmember. DOC and color measurements (absorbance at 300 nm) indicated a mid-estuary source of both. This means that although the assumption that humic substances dominate metal binding behavior seems to be correct for our samples, DOC or color measurements are not good predictors of humic content.

We also observed large salinity and pH effects on the strength of copper binding by the riverine ligands. We plan to determine whether the Biotic Ligand Model makes accurate predictions of copper binding by humic substances under these conditions. The data analysis will be completed after further calibration of our competing ligand technique, using the ligand salicylaldoxime, as a function of pH and salinity.

3. *Impacted estuaries.* In these samples, we observed the presence of both weak ligands similar to those found in the Saco River estuary, as well as copper bound in kinetically inert compounds which were not present in significant quantities in the Saco. The content of weak ligands in our samples was reasonably consistent with quantities expected from riverine inputs, but other sources of these ligands could not be ruled out. No relationship between content of weak ligands and DOC or salinity was observed. The finding of metal bound in kinetically inert forms is new for any field system, since previous methods would not have been able to distinguish between kinetically inert and strong but reversible binding. This important finding constrains the possibilities for the identity of the copper binding compounds in this system, and maybe relevant for binding of copper and other metals in other systems as well.

In summary, our results show that the Biotic Ligand Model's basic assumptions are flawed in estuarine waters. We are continuing work in Boston Harbor, to collect extensive data sets of spatial and temporal variability in the content of both kinetically inert copper and weaker ligands. These data sets will help us to determine whether an alternative approach to predicting copper complexation in estuarine waters will be feasible.

References Cited

1. Kogut, M. B. & Voelker, B. M. Strong copper binding behavior of terrestrial humic substances in seawater. *Environ. Sci. Technol.* **35**, 1149-1156 (2001).
2. Voelker, B. M. & Kogut, M. B. Interpretation of metal speciation data in coastal waters: the effects of humic substances on copper binding as a test case. *Mar. Chem.* **74**, 303-318 (2001).

Publications Resulting from this Research

Kogut, M.B. and Voelker, B.M. Kinetically inert Cu in coastal waters. *Environ Sci. Technol.*, accepted pending minor revisions.

We anticipate at least one more publication from the results of the Saco River study. However, further calibration of our competing ligand technique is needed before the data analysis can be completed.

Students Supported

Megan Brook Kogut, who completed her Ph.D. in Environmental Chemistry in MIT's Department of Civil and Environmental Engineering in June 2002, was the only student supported from this grant. Her thesis is entitled "Copper Speciation in Estuaries and Coastal Waters."